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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) PVC Moulding Compositions Stabilised by Organotin
Compounds

(72) Kaufhold, Johannes - Germany (Federal Republic of) ;
Sander, Hans J. - Germany (Federal Republic of) ;
Weinhold, Günter - Germany (Federal Republic of) ;

(71) Ciba-Geigy AG - Switzerland ;

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Notice: This application is as filed and may therefore contain an
incomplete specification.

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PVC moulding compositions stabilised by organotin compounds

Abstract

Compositions are described which comprise

- (a) 20-80 % by weight of a vinyl chloride homopolymer (PVC),
- (b) 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA,
- (c) 0.5-5 % by weight (based on (a) and (b)) of an organotin compound from the class consisting of the organotin mercaptides and/or organotin carboxylates and
- (d) 0.01-1.0 % by weight (based on (a) and (b)) of at least one perchlorate of a monovalent and/or divalent metal.

These compositions have improved heat ageing behaviour and are particularly suitable for the production of sheeting which can be employed in the motor vehicle industry.

A-19092/A/CGM 413PVC moulding compositions stabilised by organotin compounds

The invention relates to compositions comprising a vinyl halide homopolymer (PVC) and at least one copolymer, and which is stabilised by at least one organotin compound and at least one perchlorate, to the use of these compositions and to a process for stabilising PVC moulding compositions.

The preparation of flexible PVC whose stabiliser mixture contains perchlorate for the interior trim of automobiles is described, for example, in JP-A-61/34 041 and JP-A-63/57 656.

The combined use of organotin stabilisers with perchloric acid or perchlorate-containing substances is known for the preparation of rigid PVC, see, for example, JP-A-53/59 744, JP-A-61/272 258 and JP-A-01/236 252.

JP-A-62/252 445 describes plasticised PVC whose stabiliser mixture contains dimethyltin perchlorate.

A stabiliser mixture comprising the salt of a piperidine compound and perchloric acid and, if desired, a metal oxide or hydroxide, which can be used for PVC, PVC blends and halogen-free polymers is disclosed in EP-A-344 321; JP-A-59/184 240 describes a stabilised composition of PVC and a halogen-free copolymer whose stabiliser mixture likewise contains a perchlorate.

Diverse articles made from PVC blends, i.e. mixtures of PVC and a copolymer, tend to release volatile substances into the environment and undergo structural modification when exposed to elevated temperatures for extended periods. For example, motor vehicle interior trim made from said materials warms to temperatures up to 135°C when exposed to intense sunlight. Said material changes may have undesired consequences for the service properties; for example, discoloration of the material or cracks may occur. The causes of the occurrence of the undesired effects can be low effectiveness or volatility of additives, for example plasticisers or stabilisers. Chemical Abstracts 105, 116014y and

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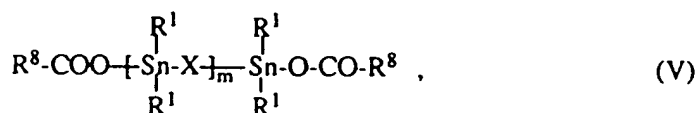
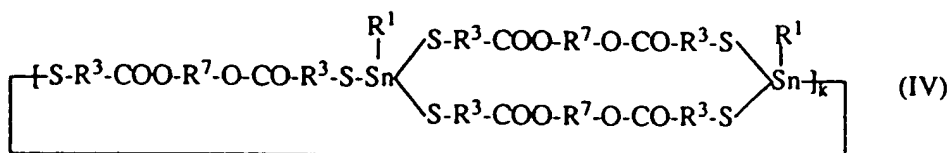
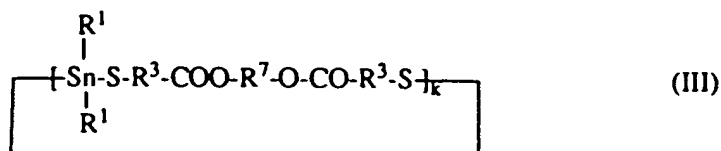
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US-A-4 954 546 therefore employ organotin compounds of reduced volatility. However, there continues to be a demand for stabilised PVC moulding compositions whose use is associated with the abovementioned disadvantages to a significantly lesser extent or not at all.

It has now been found that, surprisingly, the use of certain tin stabilisers in combination with perchlorates is capable of solving or reducing the outlined problems in articles made from some PVC blends.

The invention therefore relates to a composition comprising

- (a) 20-80 % by weight of a vinyl chloride homopolymer (PVC),
- (b) 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA,
- (c) 0.5-5 % by weight (based on (a) and (b)) of at least one organotin compound of one of the formulae I to V



in which i is the number 1 or 2, j is a number in the range from 1 to 6, k is a number in the range from 1 to 3, and m is a number in the range from 1 to 4,

R^1 is C_1 - C_{12} alkyl or C_1 - C_8 alkoxycarbonylethyl,

Q is -S- or -O-CO-,

when Q is -S-, R^2 is C_8 - C_{18} alkyl or an $-R^3$ -COO- R^4 radical, and,

when Q is -O-CO-, R^2 is C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, phenyl, C_1 - C_4 alkyl-substituted phenyl or a $-CH=CH$ -COO- R^5 radical,

R^3 is methylene, ethylene or o-phenylene,

R^4 is C_5 - C_{18} alkyl,

R^5 is C_1 - C_{18} alkyl, C_5 - C_7 cycloalkyl or benzyl,

when Q is -S-, R^6 is methylene, ethylene or o-phenylene, and,

when Q is -O-CO-, R^6 is C_1 - C_8 alkylene, o-phenylene or a $-CH=CH$ - group,

R^7 is C_2 - C_4 alkylene, or C_4 - C_8 alkylene which is interrupted by -O-,

R^8 is C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, phenyl, C_1 - C_4 alkyl-substituted phenyl or a $-CH=CH$ -COO- R^5 radical,

X is -O- and/or -O-CO- R^9 -COO-, and

R^9 is C_1 - C_8 alkylene, o-phenylene or a $-CH=CH$ - group, and

(d) 0.01-1.0 % by weight (based on (a) and (b)) of at least one perchlorate of a monovalent and/or divalent metal.

The abbreviation -COO- used above and throughout the description and in the claims denotes the $\begin{array}{c} \text{O} \\ \parallel \\ \text{-C-O-} \end{array}$ group, and the abbreviation -O-CO- denotes the $\begin{array}{c} \text{O} \\ \parallel \\ \text{-O-C-} \end{array}$ group. The abbreviations used for the copolymers are known to persons skilled in the art and are as follows:

ABS: acrylonitrile-butadiene-styrene

SAN: styrene-acrylonitrile

NBR: acrylonitrile-butadiene

NAR: acrylonitrile-acrylate

EVA: ethylene-vinyl acetate.

The composition according to the invention may contain further copolymers as modifiers. It is likewise possible to employ the abovementioned copolymers themselves in modified form. The use of modifiers, for example as blends or as graft copolymers, for improving the service properties is known to persons skilled in the art.

Alkyl R^1 , R^2 , R^4 , R^5 and R^8 in the definitions given are, for example, methyl, ethyl,

propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

C_1 - C_8 alkoxycarbonylethyl R^1 is C_1 - C_8 alkyl-O-CO-CH₂-CH₂-.

R^1 is preferably methyl, butyl or octyl, in particular butyl or octyl.

C_2 - C_{18} alkenyl R^2 and R^8 are, inter alia, ethenyl (vinyl), propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methylbut-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-heptadec-8-enyl, n-octadec-2-enyl or n-octadec-4-enyl.

C_1 - C_4 alkyl-substituted phenyl R^2 and R^8 include, for example, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl and tert-butylphenyl.

-CH=CH-COO- R^5 or -CH=CH- R^2 , R^6 , R^8 and R^9 is derived from maleic acid or fumaric acid, preferably from maleic acid.

C_5 - C_7 cycloalkyl R^5 is cyclopentyl, cyclohexyl or cycloheptyl, preferably cyclopentyl or cyclohexyl, in particular cyclohexyl.

Alkene R^6 and R^7 are a divalent alkyl radical; within the stated chain lengths, R^6 and R^7 are, for example, methylene, ethylene, -CH(CH₃)-CH₂-, -(CH₂)₃-, -(CH₂)₄-, -(CH₂)₆-, -(CH₂)₈-, -CH₂-CH(C₂H₅)-(CH₂)₄- or -CH₂-C(CH₃)₂-CH₂-; preference is given to straight-chain radicals. R^7 as C_4 - C_8 alkylene which is interrupted by -O- is, for example, -CH₂-CH₂-O-CH₂-CH₂-, -CH₂-CH₂-CH₂-O-CH₂-CH₂-CH₂-, -CH₂-CH₂-O-(CH₂)₄- or -(CH₂)₄-O-(CH₂)₄-, in particular -CH₂-CH₂-O-CH₂-CH₂-.

In the compositions according to the invention, component (c) is preferably a mixture of compounds. However, compositions in which (c) is only a single compound are also covered by the invention and have the same advantageous properties.

In the compositions according to the invention, preferred compounds of component (c) are those in which

R^1 is C_1 - C_{12} alkyl,

when Q is -S-, R^2 is C_8 - C_{18} alkyl or an - R^3 -COO- R^4 radical, and

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when Q is -O-CO-, R² is C₇-C₁₈alkyl, C₈-C₁₈alkenyl, phenyl or a -CH=CH-COO-R⁵ radical,

R³ is methylene, ethylene or o-phenylene,

R⁴ is C₅-C₁₈alkyl,

R⁵ is C₁-C₁₈alkyl or C₅-C₇cycloalkyl,

when Q is -S-, R⁶ is methylene, ethylene or o-phenylene, and,

when Q is -O-CO-, R⁶ is C₁-C₄alkylene, o-phenylene or a -CH=CH- group,

R⁷ is C₂-C₄alkylene, or C₄-C₈alkylene which is interrupted by -O-,

R⁸ is C₁-C₁₈alkyl, C₂-C₁₈alkenyl, phenyl or a -CH=CH-COO-R⁵ radical, and

R⁹ is butylene, o-phenylene or a -CH=CH- group.

Particularly preferred compounds of component (c) are those in which

R¹ is C₃-C₉alkyl,

when Q is -S-, R² is an -R³-COO-R⁴ radical, and,

when Q is -O-CO-, R² is C₇-C₁₁alkyl or a -CH=CH-COO-R⁵ radical,

R³ is methylene or ethylene,

R⁴ is C₈-C₁₈alkyl,

R⁵ is C₁-C₈alkyl or cyclohexyl,

when Q is -S-, R⁶ is methylene or ethylene, and,

when Q is -O-CO-, R⁶ is a -CH=CH- group,

R⁷ is -C₂H₄-,

R⁸ is C₈-C₁₂alkyl or a -CH=CH-COO-R⁵ radical, and,

R⁹ is a -CH=CH- group.

The -CH=CH- groups mentioned are particularly preferably cis and in the compounds are derived from maleic acid.

Compositions in which the compound(s) of component (c) are those of the formulae I, III and/or IV in which Q is -S- are likewise particularly preferred. Especially preferred compositions are those in which the compound(s) of component (c) are those of the formula I in which Q is -S-, R¹ is butyl or octyl and R² is a -CH₂-COO-R⁴- or -(CH₂)₂-COO-R⁴ radical.

The invention furthermore preferably relates to compositions in which the compound(s) of component (c) conform to the formula I, formula II and/or formula V.

Preference is given to polymer compositions in which components (a) and (b) are a mixture of 25-75 % by weight of PVC and 75-25 % by weight of said copolymers. Examples of such compositions are: 25-50 % by weight of PVC and 75-50 % by weight of copolymers, and 40-75 % by weight of PVC and 60-25 % by weight of copolymers. Preferred copolymers are ABS, SAN and modified EVA, in particular ABS. NBR, NAR and EVA are also particularly suitable. One or more of said copolymers types may be present in the composition according to the invention.

The compounds of component (d) may be perchlorates of monovalent metals, for example of alkali metals, including LiClO_4 , NaClO_4 and KClO_4 or perchlorates of divalent metals, for example of metals from the 2nd main group or subgroup of the Periodic Table, and other divalent metals, such as Pb or Cu, including $\text{Zn}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$ and $\text{Ba}(\text{ClO}_4)_2$. Component (d) can comprise a single compound or a mixture of perchlorates. Component (d) is preferably present in the compositions in an amount of from 0.05 to 1.0 % by weight (based on (a) and (b)).

In the compositions according to the invention, component (d) is preferably potassium perchlorate, sodium perchlorate, barium perchlorate, calcium perchlorate, magnesium perchlorate or zinc perchlorate, or a mixture thereof.

In the compositions according to the invention, components (c) and (d) are preferably present in an amount ratio of from 0.8 to 50 parts by weight of (c) to 1 part by weight of (d), in particular from 2 to 35 parts by weight of (c) to 1 part by weight of (d).

The compositions according to the invention may be plasticiser-free or contain conventional monomeric and/or polymeric plasticisers. Polymeric plasticisers may be, for example, the elastomers mentioned under (b). In addition, the compositions according to the invention may contain further plasticisers, for example in an amount of up to 50 % by weight, for example from 0.1 to 50 % by weight, in particular from 5 to 50 % by weight, e.g. from 10 to 40 % by weight (in each case based on the sum of components (a) and (b)). Preference is given to compositions in which component (e) is 5-50 parts by weight of a monomeric and/or polymeric plasticiser per 100 parts by weight of (a) and (b).

Suitable plasticisers are those conventional in PVC technology. Examples are given in GB-A-2 212 808, pages 4-6, and in R. Gächter/H. Müller, *Plastics Additives Handbook*, pp. 327-422, Hanser Verlag, 3rd Edition, Munich, 1990. Examples of important

monomeric plasticisers are phthalates, such as DOP (dioctyl phthalate, di-2-ethylhexyl phthalate), DINP (diisononyl phthalate), DIDP (diisodecyl phthalate) and trimellitate, such as TOTM (trioctyl trimellitate, tri-2-ethylhexyl trimellitate), TIDTM (triisodecyl trimellitate) and TITDTM (triisotridecyl trimellitate).

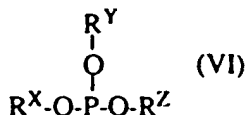
Of particular importance are compositions in which component (a) is 100 parts by weight of PVC, component (b) is 100-300 parts by weight of ABS and/or SAN-modified ABS and 0-80 parts by weight of the copolymers NBR, NAR and/or EVA, but in particular EVA, and component (e) is 5-30 parts by weight, per 100 parts by weight of (a) and (b), of further plasticisers, in particular phthalates, such as DOP, DINP and DIDP, and/or trimellitates, such as TOTM, TIDTM and TITDTM, and components (c) and (d) are as described above.

The compositions according to the invention are prepared by known processes. The stabilisers are admixed in a known manner with the polymer blends before processing. A homogeneous mixture can be obtained, for example, with the aid of known equipment at temperatures between 150 and 210°C.

The compositions according to the invention may advantageously also contain conventional amounts of further, conventional PVC stabilisers and/or further additives, for example epoxy compounds, phosphites, metal carboxylates and metal phenolates of metals from the second main group or subgroup of the Periodic Table, or alternatively inorganic salts of metals from the second subgroup of the Periodic Table, and antioxidants.

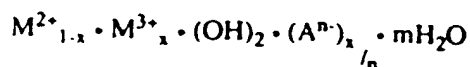
Costabilisers are preferably incorporated in amounts of from 0.05 to 6 %, in particular from 0.1 to 3 %, based on the entire composition.

Suitable conventional phosphites conform to the general formula



in which R^{X} , R^{Y} and R^{Z} are identical or different and are C_6 - C_{18} alkyl, C_6 - C_{18} alkenyl, a substituted or unsubstituted phenyl radical or C_5 - C_7 cycloalkyl.

Further costabilisers which may be mentioned are zeolites, and hydrotalcites, for example those of the formula



where

M^{2+} = Mg, Ca, Sr, Ba, Zn, Cd, Pb, Sn and/or Ni,

M^{3+} = Al, B or Bi,

A^n is an anion having the valency n,

n is a number from 1 to 4,

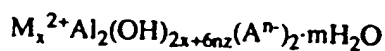
x is a number from 0 to 0.5,

m is a number from 0 to 2, and

$A = OH^-, Cl^-, Br^-, I^-, ClO_4^-, HCO_3^-, CH_3COO^-, C_6H_5COO^-, CO_3^{2-}, SO_4^{2-}$

$\begin{array}{c} COO^- \\ | \\ COO^- \end{array}$, $(CHOHCOO)_2^{2-}$, $(CHOH)_4CH_2OHCOO^-$, $C_2H_4(COO)_2^{2-}$, $(CH_2COO)_2^{2-}$, $CH_3CHOHCOO^-$, SiO_3^{2-} , SiO_4^{4-} , $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ or HPO_4^{2-} .

Other hydrotalcites which can be employed are compounds having the general formula Ia



in which M^{2+} is at least one metal from the series consisting of Mg and Zn, preferably Mg,

A^n is an anion, for example from the series consisting of CO_3^{2-} , $\begin{pmatrix} COO^- \\ | \\ COO^- \end{pmatrix}^{2-}$, OH^- and S^{2-} , where n is the valency of the anion, m is a positive number, preferably from 0.5 to 5, and x and z are positive numbers, where x is preferably from 2 to 6 and z is less than 2.

Other additional stabilisers which can be employed are metal carboxylates and phenolates of metals from the second main group or subgroup of the Periodic Table, or inorganic salts of metals from the second subgroup of the Periodic Table, for example $ZnCl_2$.

Examples of metal carboxylates are the metal salts of saturated, unsaturated or hydroxyl-substituted aliphatic carboxylic acids having 6 to 20 carbon atoms, such as

hexanoic acid, heptanoic acid, octanoic acid, 2-ethylhexanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-oxystearic acid, oleic acid, linoleic acid or ricinoleic acid. Also of interest are the metal salts of aromatic carboxylic acids, for example substituted phenyl benzoates. Preference is given to metals from the series consisting of Ba, Sr, Ca, Mg, Zn and Cd. Examples of preferred metal carboxylates are calcium stearate, zinc stearate, barium p-tert-butylbenzoate, zinc oleate and calcium oleate.

Suitable metal phenolates are, in particular, the metal salts of phenols having 6 to 20 carbon atoms, for example alkylphenols, such as p-tert-butyl-, p-octyl-, p-nonyl- and p-dodecylphenol. An example thereof is barium p-n-nonylphenolate.

Preferred antioxidants are alkylated monophenols, alkylidenebisphenols and phenyl-substituted propionic esters, but in particular 2,6-di-tert-butyl-p-cresol, 2,2-bis(4'-hydroxyphenyl)propane and n-octadecyl β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionates.

Depending on the application of the compositions according to the invention, the incorporation of the stabiliser can be preceded or accompanied by the incorporation of further additives, for example lubricants (preferably montan wax or glycerol esters), fatty acid esters, paraffins, plasticisers, fillers, carbon black, kaolin, talc, silicates, glass fibres, modifiers, optical brighteners, pigments, light stabilisers, UV absorbers, flameproofing agents and antistatics.

Preferred such additives are lubricants, pigments, processing assistants, fillers, antioxidants and/or light stabilisers.

Of particular practical importance are compositions according to the invention which do not contain any hindered amines, in particular none of the polyalkylpiperidine type.

Components (c) and (d) of the compositions according to the invention and optional additives can also be added to the polymers to be stabilised in the form of a masterbatch. The latter can comprise, for example, from 10 to 40 % by weight of component (c), from 1 to 20 % by weight of component (d), and polymers of component (a) or (b), costabilisers, such as hydrotalcites, plasticisers, processing assistants, fillers or a combination of these.

The compositions according to the invention can be converted into mouldings by shaping methods which are customary for this purpose, e.g. by injection moulding, calendaring or extrusion, in particular flat-film extrusion.

The compositions according to the invention are preferably used for the production of hollow articles and sheeting for the motor vehicle industry. This use is likewise covered by the invention. A particularly preferred area of application is the production of sheeting for the interiors of motor vehicles, which is known as crash-pad sheeting, in particular as described in DE-A-3 227 107 and DE-A-3 401 452.

The compositions according to the invention are particularly advantageously used for the production of thermoformed and flexible sheeting based on PVC, in particular for use in the motor vehicle industry.

As is known from the chemistry of organotin stabilisers, the latter are frequently present in the stabilised substrate in a different form from that in which they were added. Reaction (comproportionation) products are formed. The invention naturally also relates to compositions which contain products formed from the compounds of component (c), conforming to the formulae I to V.

The organotin compounds of the formulae I to V are known (see, for example, the references cited in the introduction).

In addition to the compounds of component (c) of the formulae I to V, further tin stabilisers may be present in the compositions according to the invention so long as they do not adversely affect the improved properties achieved by said compounds. However, preference is given to compositions according to the invention which contain no further tin stabilisers in addition to the above-described organotin compounds of component (c) and the comproportionation products thereof.

The invention furthermore relates to the use of the organotin compounds of component (c) in combination with the perchlorates of monovalent and/or divalent metals defined above as component (d) for stabilising moulding compositions comprising 20-80 % by weight of a vinyl chloride homopolymer (PVC) and 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA, against damage by heat and light. This also includes a process for stabilising moulding compositions comprising

(a) 20-80 % by weight of a vinyl chloride homopolymer (PVC) and (b) 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA against damage by heat and light, which comprises adding to the compositions (per 100 parts by weight of (a) and (b)) 0.5-5 parts by weight of at least one of the organotin compounds defined above as component (c) in combination with 0.01-1.0 part by weight (per 100 parts by weight of (a) and (b)) of at least one of the perchlorates of monovalent and/or divalent metals defined above as component (d).

The examples below (long-term exposure of films to heat and measurement of the discoloration) describe the invention in greater detail. Parts and percentages therein, as in the remainder of the description and in the claims, are based on the weight of the sum of components (a) and (b), unless stated otherwise.

Example 1:

A mixture of

- 50.0 parts by weight of S-PVC (K value 70),
- 30.0 parts by weight of ABS (Blendex[®] 101, General Electric Corp.),
- 30.0 parts by weight of SAN-modified ABS (Bayer, Grade KL 2065),
- 10.0 parts by weight of modified EVA (Elvaloy[®], Du Pont),
- 15.0 parts by weight of trimellitic esters (plasticiser, Grade REOMOL[®] LTM, Ciba-Geigy Marienberg GmbH),
- 3.0 parts by weight of rutile (Kronos RN 57P) and
- 2.5 parts by weight of organotin stabiliser comprising
 - 25 % by weight of $C_4H_9Sn(S-CH_2-COO-i-C_8H_{17})_3$ and
 - 75 % by weight of $(C_4H_9)_2Sn(S-CH_2-COO-i-C_8H_{17})_2$ ($i-C_8H_{17}$ here is a mixture of various isomeric octyl radicals)

is rolled out in a conventional manner on mixing rolls for 5 minutes at a temperature of 190°C to give a 0.4 mm thick sheet. Pieces of this sheet measuring 4x4 cm are stored in a drying cabinet at 120°C with the test specimens suspended so that both sides of the sheet are free. Test specimens are removed at intervals of 72 hours in order to determine the colour difference in accordance with DIN 5033 (Experiment I, comparison).

For Experiment II (composition according to the invention), 0.08 part by weight of sodium perchlorate is additionally added to the abovementioned mixture. The mixture is subsequently processed and tested in the same way.

The measurement results (colour difference according to DIN 5033 and DIN 6174) are shown in Table 1 below. The greater the colour difference, the greater the discoloration.

Table 1: Colour difference in test specimens after storage at 120°C

| Experi- ment | Colour difference ΔE (according to DIN 5033/ DIN 6174) after | | | | | | | |
|-----------------|---|------|-------|-------|-------|-------|-------|-------|
| | 0 h | 72 h | 144 h | 216 h | 288 h | 360 h | 432 h | 504 h |
| I | 10.6 | 18.3 | 25.7 | 27.9 | 30.3 | 33.4 | 34.8 | 36.4 |
| II | 12.2 | 17.5 | 22.0 | 23.3 | 26.0 | 28.1 | 29.4 | 31.6 |

The measurement results show a relatively small colour difference for the composition according to invention after heating, which indicates a better thermostabilising action than the perchlorate-free composition.

Example 2:

Mixtures comprising:

50.0 parts by weight of S-PVC (K value 70),

30.0 parts by weight of ABS (Blendex[®] 101, General Electric Corp.),

30.0 parts by weight of SAN-modified ABS (Bayer, Grade KL 2065),

10.0 parts by weight of modified EVA (Elvaloy[®], Du Pont),

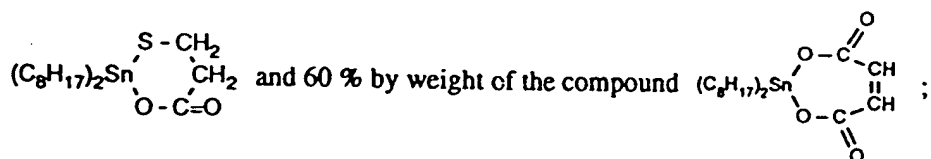
15.0 parts by weight of trimellitic esters (plasticiser, Grade REOMOL[®] LTM, Ciba-Geigy Marienberg GmbH),

3.0 parts by weight of rutile (Kronos RN 57P) and

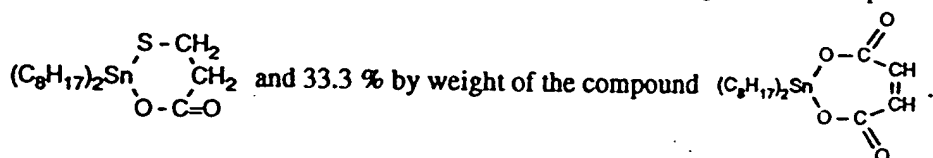
1.5 parts by weight of the organotin stabiliser A or B described below

are prepared and tested by the method described in Example 1 (Experiments I and III, comparison).

Organotin stabiliser A is a mixture comprising 40 % by weight of the compound



organotin stabiliser B is a mixture comprising 66.7 % by weight of the compound



For Experiments II and IV, 0.13 part by weight of $NaClO_4$ is in each case additionally added to the mixture described (compositions according to the invention).

Test specimens are removed at intervals of 48 hours in order to determine the colour difference in accordance with DIN 5033.

The measurement results (colour difference in accordance with DIN 5033 and DIN 6174) are shown in Table 2 below. The greater the colour difference, the greater the discoloration.

Table 2: Colour difference in test specimens after storage at 120°C

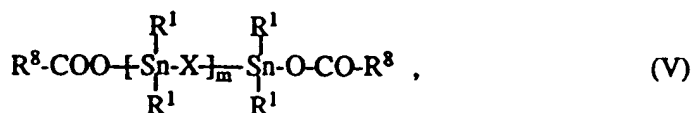
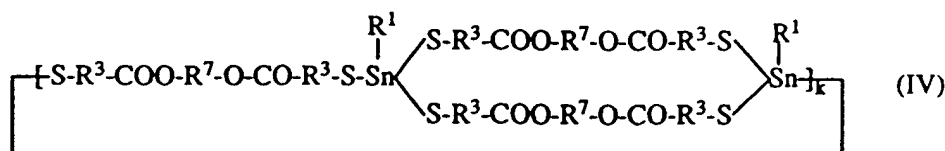
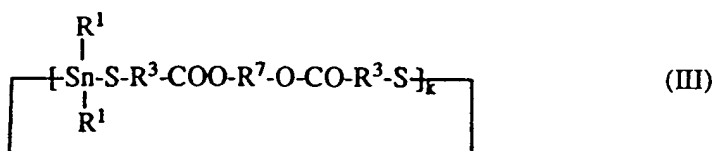
| Colour difference ΔE (according to DIN 5033/ DIN 6174) after | | | | | | | | | | |
|---|------|------|------|------|------|------|------|------|------|------|
| Experi- ment | 0h | 48h | 96h | 144h | 192h | 240h | 288h | 336h | 384h | 432h |
| I | 11.4 | 19.1 | 22.4 | 31.4 | 33.1 | 39.5 | 44.0 | 48.0 | 49.9 | 51.3 |
| II | 11.2 | 18.1 | 20.9 | 26.8 | 27.0 | 30.2 | 33.6 | 35.6 | 37.0 | 38.1 |
| III | 11.2 | 20.7 | 24.0 | 32.9 | 35.1 | 40.6 | 45.6 | 47.7 | 49.9 | 51.3 |
| IV | 11.6 | 20.5 | 22.5 | 27.1 | 27.5 | 30.7 | 33.7 | 35.3 | 37.1 | 36.0 |

The measurement results show a significantly smaller colour difference for the compositions according to the invention after heating.

WHAT IS CLAIMED IS:

1. A composition comprising

- (a) 20-80 % by weight of a vinyl chloride homopolymer (PVC),
 (b) 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA,
 (c) 0.5-5 % by weight (based on (a) and (b)) of at least one organotin compound of one of the formulae I to V



in which i is the number 1 or 2, j is a number in the range from 1 to 6, k is a number in the range from 1 to 3, and m is a number in the range from 1 to 4,

R^1 is C_1 - C_{12} alkyl or C_1 - C_8 alkoxycarbonylethyl,

Q is -S- or -O-CO-,

when Q is -S-, R^2 is C_8 - C_{18} alkyl or an $-R^3-COO-R^4$ radical, and,

when Q is -O-CO-, R^2 is C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, phenyl, C_1 - C_4 alkyl-substituted phenyl or a $-CH=CH-COO-R^5$ radical,

R^3 is methylene, ethylene or o-phenylene,

R^4 is C_5 - C_{18} alkyl,

R^5 is C_1 - C_{18} alkyl, C_5 - C_7 cycloalkyl or benzyl,
 when Q is -S-, R^6 is methylene, ethylene or o-phenylene, and,
 when Q is -O-CO-, R^6 is C_1 - C_8 alkylene, o-phenylene or a -CH=CH- group,
 R^7 is C_2 - C_4 alkylene, or C_4 - C_8 alkylene which is interrupted by -O-,
 R^8 is C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, phenyl, C_1 - C_4 alkyl-substituted phenyl or a
 -CH=CH-COO- R^5 radical,
 X is -O- and/or -O-CO- R^9 -COO-, and
 R^9 is C_1 - C_8 alkylene, o-phenylene or a -CH=CH- group, and
 (d) 0.01-1.0 % by weight (based on (a) and (b)) of at least one perchlorate of a monovalent
 and/or divalent metal.

2. A composition according to claim 1, in which, in the compounds of component (c),

R^1 is C_1 - C_{12} alkyl,
 when Q is -S-, R^2 is C_8 - C_{18} alkyl or an - R^3 -COO- R^4 radical, and,
 when Q is -O-CO-, R^2 is C_7 - C_{18} alkyl, C_8 - C_{18} alkenyl, phenyl or a -CH=CH-COO- R^5
 radical,
 R^5 is C_1 - C_{18} alkyl or C_5 - C_7 cycloalkyl,
 when Q is -O-CO-, R^6 is C_1 - C_4 alkylene, o-phenylene or a -CH=CH- group,
 R^8 is C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, phenyl or a -CH=CH-COO- R^5 radical, and
 R^9 is butylene, o-phenylene or a -CH=CH- group.

3. A composition according to claim 2, in which, in the compounds of component (c)

R^1 is C_3 - C_9 alkyl,
 when Q is -S-, R^2 is an - R^3 -COO- R^4 radical, and,
 when Q is -O-CO-, R^2 is C_7 - C_{11} alkyl or a -CH=CH-COO- R^5 radical,
 R^3 is methylene or ethylene,
 R^4 is C_8 - C_{18} alkyl,
 R^5 is C_1 - C_8 alkyl or cyclohexyl,
 when Q is -S-, R^6 is methylene or ethylene, and,
 when Q is -O-CO-, R^6 is a -CH=CH- group,
 R^7 is - C_2H_4 -,
 R^8 is C_8 - C_{12} alkyl or a -CH=CH-COO- R^5 radical, and,
 R^9 is a -CH=CH- group.

4. A composition according to claim 3, in which the compound(s) of component (c) is(are)
 of the formulae I, III and/or IV in which Q is -S-.

5. A composition according to claim 3, in which the compound(s) of component (c) conform(s) to the formula I, formula II and/or formula V.
6. A composition according to claim 1, in which component (a) is 25-50 % by weight of PVC and component (b) is 75-50 % by weight of at least one of the copolymers mentioned in claim 1.
7. A composition according to claim 1, in which component (a) is 40-75 % by weight of PVC and component (b) is 60-25 % by weight of at least one of the copolymers mentioned in claim 1.
8. A composition according to claim 1, in which component (d) is potassium perchlorate, sodium perchlorate, barium perchlorate, calcium perchlorate, magnesium perchlorate and/or zinc perchlorate.
9. A composition according to claim 1, additionally containing, per 100 parts by weight of (a) and (b),
(e) 5-50 parts by weight of a monomeric and/or polymeric plasticiser.
10. A composition according to claim 1, additionally containing lubricants, pigments, processing assistants, fillers, antioxidants and/or light stabilisers.
11. A composition according to claim 1, containing no further tin stabilisers in addition to the organotin compounds of component (c) and the comproportionation products thereof.
12. A composition according to claim 1 in form of a sheeting or hollow article for the motor vehicle industry.
13. The use of an organotin compound as defined in claim 1 as component (c) in combination with a perchlorate of a monovalent and/or divalent metal defined in claim 1 as component (d) for stabilising moulding compositions comprising 20-80 % by weight of a vinyl chloride homopolymer (PVC) and 80-20 % by weight of at least one copolymer of the group consisting of ABS, NBR, NAR, SAN and EVA, against damage by heat and light.

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14. A process for stabilising moulding compositions comprising (a) 20-80 % by weight of a vinyl chloride homopolymer (PVC) and (b) 80-20 % by weight of at least one copolymer from the group consisting of ABS, NBR, NAR, SAN and EVA, against damage by heat and light, which comprises adding to the compositions (per 100 parts by weight of (a) and (b)) 0.5-5 parts by weight of at least one of the organotin compounds defined in claim 1 as component (c) in combination with 0.01-1.0 part by weight (per 100 parts by weight of (a) and (b)) of at least one of the perchlorates of monovalent and/or divalent metals defined in claim 1 as component (d).

**Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents**